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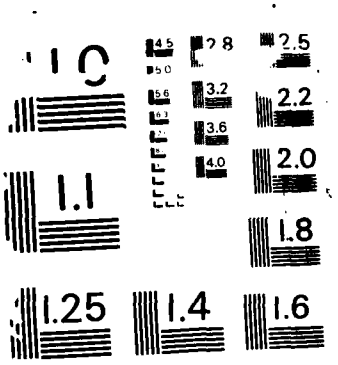

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This final report summarizes three years of research on the ion-molecule chemistry of phosphorus and sulfur compounds in the gas phase. A new instrument, the tandem flowing afterglow-SIFT-drift, has been successfully designed and constructed; the instrument has exceptional sensitivity, resolution and versatility. New techniques have been developed for the preparation of reactive phosphorus and sulfur species. The gas phase chemistry of energy-rich ions and neutrals has been studied. (8 pages)

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ARO REPORT NO. 18

GAS PHASE ION-MOLECULE CHEMISTRY OF PHOSPHORUS & SULFUR COMPOUNDS

FINAL REPORT

CHARLES H. DEPUY
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March 18, 1988

Contract No. DAAG29-85-K-0046

UNIVERSITY OF COLORADO
BOULDER, COLORADO 80309-0215

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Summary of the Research Problem

A. STATEMENT OF THE PROBLEM STUDIED

Our overall objective in this research was to develop methods by which the gas phase ion-molecule chemistry of phosphorus and sulfur compounds can be compared with that of their first-row counterparts, analogous compounds of nitrogen and oxygen. This has involved two aspects, one the construction of a new instrument in which ions of these elements can be prepared and reacted and, second, the development of new methods for the preparation of neutral reactants for study. In the first of these objectives we have been spectacularly successful and in the second a great deal of progress has been made.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

Overall views of our research into gas-phase ion molecule reactions are contained in three review articles (Ref. 6, 7, 12). The major instrumental advance was the successful construction of the flowing afterglow selected ion flow-drift tube (FA-SIFT-Drift). A schematic of this instrument is given in Figure I and more details of its operation are given in published articles (Ref. 9, 13). Briefly, ions are produced in a flowing afterglow by either direct electron impact or by ion-molecule synthetic pathways. At the end of this first FA the ion plasma is sampled into a low-pressure quadrupole region, the neutrals are removed by pumping and ions of the desired mass-to-charge ratio are selected in a quadrupole mass filter and injected into a second FA. In this second flow tube the reactions of these ions can be studied without complications from the presence of other ions, electrons, photons or precursor neutrals. The instrument has proven to have extremely high selectivity and sensitivity so

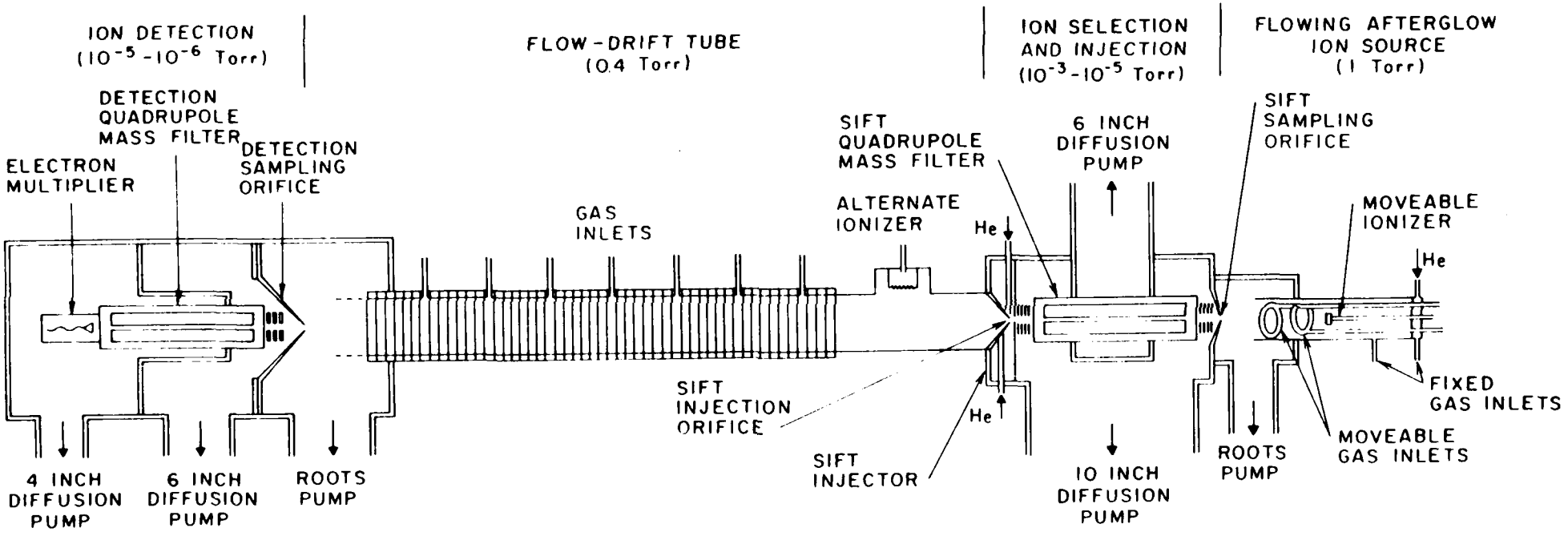
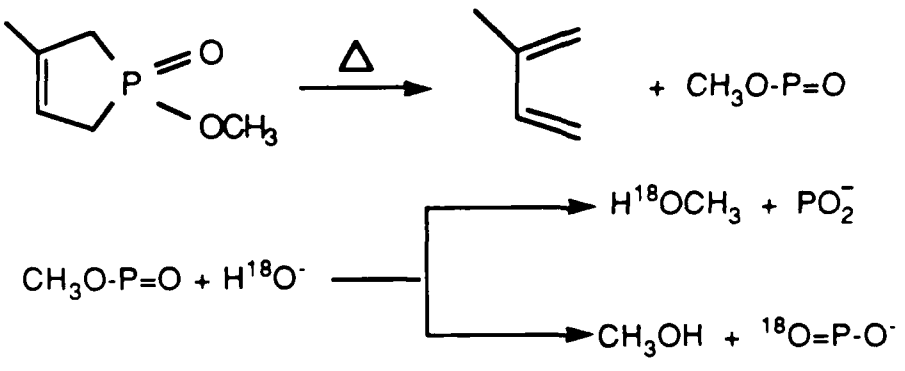


Figure 1. The Tandem Flowing Afterglow-SIFT-Drift Instrument.

that, for example, isotopically labelled ions can often be injected from unenriched neutral precursors, merely relying on the natural abundance of such isotopes as ^{18}O (0.25%) (Ref. 9), ^{13}C (1.1%) or ^{15}N (0.5%). Highly reactive and/or unusual ions like CH_2^- (Ref. 10), $HCSi^-$ or PO_3^- can also be prepared and studied. The development of this instrument has enormously extended our ability to investigate gas-phase ion-molecule chemistry.

Simultaneously we have been developing methods by which highly reactive neutral molecules can be generated in the gas phase so that their ion chemistry can be investigated. Our previous studies of gas phase ion chemistry have convinced us that there is usually a very good correlation between the reaction pathways observed in the gas phase and those seen in solution. Thus, if we can investigate the gas phase ion chemistry of these unusual species, we can predict how they will react in solution. We have therefore equipped our flowing afterglow apparatus with a pyrolyzer. Appropriate precursors are allowed to flow through this furnace at which times they decompose with the formation of the desired neutral. They then flow directly into the FA where they are cooled by collisions with helium and allowed to react with anions. An example is shown below:



Neither methyl metaphosphite nor the metaphosphite ion has ever been studied previously in the gas phase or in solution. These studies are presently being prepared for publication.

In parallel with these investigations we have been studying the gas phase ion chemistry of a number of energy-rich ions and neutrals including COS and CS_2 (Ref. 1), $CH_2{=}N^-$ (Ref. 2), N_2O (Ref. 3), HO_2^- (Ref. 4), CH_2N_2, CH_3NC (Ref. 11), and others. We have investigated the mechanisms of alkane eliminations in exothermic reactions of organosilanes, both by theory and experiment (Ref. 5, 8). We have also studied the gas phase chemistry of CH_3PH_2 and CH_3PH^-. In addition we have carried out studies of the substitution reactions of $(CH_3)PCl$ with a series of nucleophiles in order to explore the pathway by which such analogs of S_N2 reactions occur on phosphorus. As was the case for silicon, also a second row element, it appears that an intermediate anion $[(CH_3)_2Cl\,\bar{P}Nu]$ is formed during the reaction. We have also carried out mechanistic studies on phosphorus and sulfur esters to investigate how hydrolysis proceeds in the gas phase.

In summary, our three years of ARO sponsorship have been extremely exciting and productive. This research has resulted in thirteen publications with four additional manuscripts currently in preparation.

C. ARO SPONSORED PUBLICATIONS

1. "Fragmentation of Organic Anions Induced by Exothermic Addition Reactions", C. H. DePuy, *Org. Mass Spectrometry*, **1985**, 20, 556-559.

2. "Gas-Phase Ion Chemistry of Azides. The Generation of $CH_2{=}N^-$ and $CH_2{=}NCH_2^-$ ", S. R. Kass and C. H. DePuy, *J. Org. Chem.*, **1985**, 50, 2874-2877.

3. "Nitrous Oxide in Gas Phase Ion-Molecule Chemistry: A Versatile Reagent for the Determination of Carbanion Structure", S. R. Kass, J. Filley, J. M. Van Doren, C. H. DePuy, *J. Am. Chem. Soc.*, **1986**, 108, 2849-2852.

4. "Gas Phase Reactions of the Hydroperoxide and Peroxyformate Anions", J. H. Bowie, C. H. DePuy, S. A. Sullivan and V. M. Bierbaum, *Can. J. Chem.*, **1986**, 64, 1046-1050.

5. "The Gas Phase Negative Ion Chemistry of Organosilanes", *Acc. Chem. Res.*, **1987**, 20, 127-133.

6. "Formation of Anions in the Gas Phase", C. H. DePuy and V. M. Bierbaum, in "Structure/Reactivity and Thermochemistry of Ions", P. Ausloos and S. G. Lias (eds.); D. Reidel: Dordrecht, Holland, 1987; pp. 279-291.

7. "Proton Transfer Reactions of Anions", C. H. DePuy and V. M. Bierbaum, in "Structure/Reactivity and Thermochemistry of Ions", P. Ausloos and S. G. Lias (eds.); D. Reidel: Dordrecht, Holland, 1987; pp. 293-303.

8. "The Mechanisms of Alkane Eliminations from the Intermediates produced by Reactions of the Hydroxide and Methoxide Negative Ions with Tetramethylsilane in the Gas Phase", J. C. Sheldon, R. N. Hayes, J. H. Bowie and C. H. DePuy, *J. Chem. Soc., Perkin Trans. II*,, **1987**, 275-280.

9. "Tandem Flowing Afterglow-Selected Ion Flow Tube and Its Application to the Thermal Energy Reactions of $^{18}O^-$", J. M. Van Doren, S. E. Barlow, C. H. DePuy and V. M. Bierbaum, *J. Am. Chem. Soc.*, **1987**, 109, 4412-4414.

10. "Gas Phase Chemistry of $CH_2^{\bullet -}$ ", C. H. DePuy, S. E. Barlow, J. M. Van Doren, C. R. Roberts and V. M. Bierbaum, *J. Am. Chem. Soc.*, **1987**, 109, 4414-4415.

11. "Gas Phase Negative Ion Chemistry of Methylisocyanide", J. Filley, C. H. DePuy and V. M. Bierbaum, *J. Am. Chem. Soc.* **1987**, 109, 5992-5995.

12. "Ion Molecule Reactions in a Flowing Afterglow and SIFT", C. H. DePuy and V. M. Bierbaum, *Spectros. Int. J.* **1987**, 5, 95-100.

13. "The Tandem Flowing Afterglow-SIFT-Drift", J. M. Van Doren, S. E. Barlow, C. H. DePuy and V. M. Bierbaum, *Int. J. Mass Spectrom. Ion Proc.* , **1987**, 81, 85-100.

D. PARTICIPATING SCIENTIFIC PERSONNEL

Charles H. DePuy, Professor of Chemistry, Principal Investigator.

Veronica M. Bierbaum, Senior Research Associate, Co-Principal Investigator.

Christopher R. Roberts, post-doctoral research associate.

Amy S. Mullin, graduate student

Jane M. Van Doren, graduate student; Ph.D. awarded May, 1987.

Stephan E. Barlow, postdoctoral research associate.

Jonathan Filley, graduate student; Ph.D. awarded 1985.

Steven R. Kass, postdoctoral research associate.

Brad McGarvey, undergraduate research assistant.

END

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